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THALLIUM

BY

ALICE V. PETAR

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CONTENTS

	Page
Introduction	1
Description and properties	2
History	2
Occurrence	3
Uses	3
Production	5
Markets and prices	5
Bibliography	5

INTRODUCTION

Thallium is one of the rare metals that has come into commercial use within recent years. Its comparative scarcity, combined with a resemblance to the common metal lead, have retarded the development of uses for thallium. Although production is still measured in pounds rather than in tons, it is now finding application in a number of fields. Perhaps the earliest commercial use of thallium was as a constituent of optical glass of higher refractive power than similar glasses containing lead. One of the later applications to attract attention was the use of the oxysulphide in a sensitive electrical device similar to the selenium cell. The "Thalofide" cell, which was patented in 1919, constituted for a time the most important outlet for thallium. During the next few years the limited use of thallium and its salts in other fields was insufficient to absorb an annual production of a few hundred pounds, and the price dropped from $16 or $18 per pound in 1922 to $5 per pound in 1924. Beginning in 1925 several new uses were developed, especially as a poison for rodents and ants, and as a result the demand for thallium increased sufficiently to cause a recovery in price to the present level of from $12 to $15 per pound.

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[1] - The Bureau of Mines will welcome reprinting of this article, provided the following footnote acknowledgment is used: "Reprinted from U. S. Bureau of Mines Information Circular 6453."

[2] - Rare metals and nonmetals division, U. S. Bureau of Mines.

There are no commercial ores of thallium, although it is present in small quantities in a great many minerals. The supply was formerly obtained solely from flue dusts that accumulate in sulphuric acid plants where pyrite is used. The thallium content of these flue dusts is small, -- usually about half of 1 per cent, -- and the thallium is produced only as a by-product. According to information contained in a letter from L. G. Matthews, of the American Smelting and Refining Co., to the Bureau of Mines, at present most of the domestic supply is a by-product of the purification of cadmium ,itself a by-product of the smelting of other metals.

DESCRIPTION AND PROPERTIES

The physical and chemical properties of thallium are very similar to those of lead. The metal is white with a bluish-gray tinge, somewhat paler than lead. It has a bright metallic luster when freshly cut but dulls quickly when exposed to air. Thallium is softer than lead; it can be scratched by the finger nail and is easily cut with a knife. It is malleable but has little tenacity, and can be squeezed (extruded) but not drawn, into wire. A number of determinations have been made for the melting point of thallium, ranging from 204.05 to 303.7°C., but 303.5°C. has been accepted by the International Critical Tables. According to A. Lamy the specific gravity of thallium is 11.862, although slight variations from this figure have been given by other investigators. The metal has a crystalline structure and when bent gives forth a sound like the "cry of tin." Thallium amalgamates with mercury and forms alloys with many other metals. It is slowly soluble in alcohol, insoluble in liquid ammonia, and combines directly with sulphur, phosphorus, and the halogens.

HISTORY

The discovery of thallium dates back to the early part of 1861, when W. Crookes noted a bright line in the spectrum of the selenium residues from a sulphuric acid factory in the Harz Mountains. He was looking for tellurium, but spectroscopic examination revealed the presence of an unknown element, to which he gave the name "thallium," - "from the Latin thallus, a budding twig - a word which is frequently employed to express the beautiful green tint of young vegetation; and which I have chosen because the green line which it communicates to the spectrum recalls with peculiar vividness the fresh color of vegetation in spring." He announced the discovery on March 30, 1861, in a paper "On the Existence of a New Element, Probably of the Sulphur Group." Crookes was at first hampered by a lack of material, but in the course of a year he was able to collect a few grains of the metal in powder form.

In May 1862 A. Lamy observed the green spectral line from the chamber deposit of a sulphuric acid plant where Belgian pyrites were roasted. Lamy obtained several hundred grams of the metal and was able to make considerable progress in determining the chemical and physical properties of the new element. Subsequently H. L. Wells, S. L. Penfield, and other investigators studied the metal and its properties. Thallium continued as an object of scientific interest, but only within the last decade have its commercial possibilities been recognized.

OCCURRENCE

Four very rare minerals contain appreciable percentages of thallium. Crookesite, a thallium-copper-silver-selenide, $(CuTlAg)_2Se$, which contains from 16 to 19 per cent of thallium, is found in Skrikerum, Sweden. Lorandite, a sulphide of thallium and arsenic, $TlAsS_2$, contains from 59 to 60 per cent of thallium and is found in Macedonia. Hutchinsonite, a sulphoarsenide of thallium, lead, silver, and copper approximating $(Tl,Ag,Cu)_2S.PbS.2As_2S_3$, has a thallium content of from 18 to 25 per cent. This mineral occurs in white dolomite of the Lengenbach Quarry in the Binnental, Switzerland. Vrbaite, found in Macedonia, is a sulphide of thallium, arsenic, and antimony $(TlAs_2Sb_5)$ which contains 29 to 32 per cent of thallium.

Thallium is also present in small quantities in a great variety of rocks and minerals, such as pyrites, zinc blende, hematite, lepidolite, muscovite, orthoclase, pitchblende, berzelinite, frenzelite, pyrolusite, manganite, carnallite, etc. Owing to its occurrence in some of the common minerals, thallium is found in commercial products such as zinc, cadmium, platinum, bismuth, tellurium, and sulphuric acid. Copper pyrites and iron pyrites frequently contain thallium, and the flue dusts from sulphuric acid plants where thalliferous pyrites are burned have constituted one of the principal sources of supply. The thallium content of such flue dusts is usually less than half of 1 per cent, but in some instances a content as high as 7 per cent has been noted.

USES

Alloys of lead and thallium are somewhat unusual in that they have higher melting points than either of the component metals; they are used in rather small quantities in special types of electrical fuses. An alloy containing 10 per cent thallium, 20 per cent tin, and 70 per cent lead is resistant to the corrosive action of mixtures of sulphuric, nitric, and hydrochloric acids. This alloy has been recommended for use as an anode for the electrolytic deposition of copper, since its corrosion is less than one-fifth that of lead alone.[3]

In a discussion of the possibility of using lead-base bearing metal in place of tin-base, O. W. Ellis[4] reports that the results of experiments indicate that the addition of thallium to lead-base alloys markedly improves their resistance to deformation; and that yield point and ultimate strength tests show that an alloy containing lead 72, antimony 15, tin 5, and thallium 8, is superior to the best tin-base bearing alloy.

Silver alloys containing as much as 22 per cent thallium have been patented by I. G. Farbenind A.-G.[5]

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3 - Hopkins, B. Smith, Chemistry of the Rarer Elements: D. C. Heath & Co., New York, N. Y., 1923, pp. 125-126.

4 - Ellis, O. W. Increasing the strength of lead-base bearing metals. Am. Metal Market, vol. 35, 1928, pp. 1-4, 44.

5 - I. G. Farbenind, A.-G., Silver alloys resistant to chemical action. Brit. Pat. 297,665, June 30, 1927.

Many uses have been found for thallium compounds. By far the most important commercial outlet for the element is the utilization of thallium sulphate as a poison for rodents and as an insecticide for ants. The sulphate has the advantage of being tasteless and odorless. Ernest G. Enck[6] has described several formulas that are said to be effective as poison bait for field mice. In one, 1½ pounds of thallium sulphate are dissolved in 6 quarts of boiling water, and ½ pound of starch, which has been mixed in a little cold water, is added. The mixture is boiled two or three minutes, then ½ pint of glycerine is added, and the boiling is continued for a few minutes longer. In another method 2½ per cent of thallium sulphate is added to a tapioca flour and made into a paste, which is spread on sliced bread. A third recipe calls for ¼ ounce of thallium sulphate, which is dissolved in a large teacup of water and brought to a boil. To this is added ½ cup of corn syrup and 12 ounces of peanut butter, which may be spread on two ordinary sized loaves of bread sliced quite thin. The slices are then cut in small squares. It is said that noticeable results should be seen at about the third day after placing.

A syrup prepared by boiling together 1 pint of water, 1 pound of sugar, 27 grains of thallium sulphate, and 3 ounces of honey, is said to be effective in exterminating a species of red ants which arsenic syrups failed to control. The thallium appears to act as a slow cumulative poison. In a number of houses and apartments the entire colony was destroyed within three weeks to a month. The pavement ant is even more readily controlled.[7]

Because of their high refracting power, thallium compounds are used in the manufacture of certain kinds of optical glass in which a high refractive index is required.

The oxysulphide of thallium is used in the "Thalofide" cell, which is more sensitive to light, especially that of low intensity and long wave lengths, than the selenium cell. Its electric resistance drops 50 per cent on exposure to a quarter-foot candle. Several patents for the "Thalofide" cell were issued to Theodore W. Case in 1919 and 1920. Mr. Case has also patented a compound of thallium and bromine (U. S. Patent 1,342,842, June 8, 1920) which is used as an electric resistance material in the Bellphotophone or similar apparatus.

The use of thallium and its compounds to prevent knocking in internal combustion engines has been patented.[8] According to the patent specifications, thallium or thallium oxide may be vaporized outside the cylinder by an electric arc or a thallium compound may be mixed with the fuel or otherwise injected into the engine. The compounds which may be used include thallium ethyl, benzylate, phenylethylate, oleate, amylalcoholate, and acetoacetate.

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6 - Enck, Ernest G., Thallium and its Uses: Foote-Prints, vol. 2, No. 1, 1929, pp. 15-17.

7 - Popenoe, C. H., Thallium as an Insecticide: Science, vol. 64, 1926, p. 525.

8 - Asiatic Petroleum Co., Ltd., and Egerton, A. C., Use of thallium and its compounds to prevent knocking in internal combustion engines. Brit. Pat. 279,560, July 29, 1926.

A liquid amalgam containing 8.5 per cent of thallium has been used in thermometers for recording temperatures as low as -60°.

Thallous chloride has found use as a "getter" in tungsten lamp to prolong the life of the filament. It is one of the few lower chlorides is more stable than the compound of the higher state of oxidation.

In a study of heavy liquids for mineralogical analyses[9] the Bureau of Mines found that the most suitable liquid for sink-and-float work on minerals of high specific gravity was a water solution of the double thallous formate-malonate. This double salt, with a specific gravity of 4.9, melts at 60° C. and is miscible in all proportions with water. At room temperatures the salt is soluble enough to give a solution with a specific gravity of nearly 4.3. As a liquid of intermediate gravity, an aqueous solution of thallous formate is recommended. It is less expensive than the formate-malonate. A maximum specific gravity of 3.5 is reached at room temperatures, and gravities up to 4.95, the gravity of the molten salt, may be obtained.

Thallium acetate has been used for the treatment of certain kinds of tuberculosis and ringworm. At one time it was used as a depilatory.

PRODUCTION

At present thallium is produced in the United States by only one company, the American Smelting & Refining Co., which recovers the metal as a by-product in its cadmium operations.

MARKETS AND PRICES

The demand for thallium and its salts is not large. The only compound of thallium that has attained any marked commercial development is the sulphate, and it is understood that this demand is being taken care of largely by importations from Germany. No figures covering imports are available.

Early in 1931 thallium metal was quoted at from $12.50 to $15 per pound, and the sulphate was selling at prices ranging from $10 to $15 per pound.

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[9] - Sullivan, John D., Heavy Liquids for Mineralogical Analyses: Tech. Paper 381, Bureau of Mines, 1927, 25 pp.

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